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EFFECT OF TRIPLET CORRELATIONS ON THE ADSORPTION OF A
DENSE FLUID ONTO A CRYSTALLINE SURFACE

by

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**Effect of Triplet Correlations on the Adsorption of a Dense Fluid
onto a Crystalline Surface**

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The adsorption of a fluid of hard spheres of diameter σ onto a planar surface containing a triangular lattice of adsorption sites, spacing σ , was studied using a model which is equivalent to a lattice gas with n-body interactions that are related to the n-body correlation functions of the fluid. The present paper extends our previous work, which included only pairwise interactions, to also include triplet interactions. We discovered a simple but accurate analytical approximation to the triplet correlation function for three spheres in mutual contact, which, when combined with a Müller-Hartmann and Zittarz approximation of the critical point in the equivalent lattice gas, yields the estimate $\rho_c \sigma^3 = 0.8409$ of the fluid density at the critical point of the condensation transition which occurs at the fluid-crystal interface. This estimate, which includes the effects of both pair and triplet correlations in the fluid, is significantly higher than the value $\rho_c \sigma^3 = 0.6678$ obtained if only the effects of pair correlations are included in the calculation.

I. Introduction

In the present paper we calculate the effect of three-body correlations on the critical point for two-phase coexistence in a model for the adsorption of a dense fluid onto a crystalline surface. The model,¹ described in Sec. II, is equivalent to a two-dimensional lattice gas with n -body interactions which are related to the n -body correlations in the fluid at the surface.

In a previous paper² we used the model to calculate the two-phase coexistence curve for a fluid of hard spheres of diameter σ near a smooth, hard wall containing a triangular lattice of sticky sites with a first-neighbor spacing σ . We used the Kirkwood superposition approximation³ to estimate the n -body correlation functions of the fluid at the wall as a product of pair correlation functions. Using the Percus-Yevick (PY) virial approximation to the pair correlation function,^{4,5} together with the exact two-phase coexistence curve for the equivalent lattice gas with pairwise interactions, we calculated that the critical point of the two-phase coexistence surface occurs at $\rho_c \sigma^3 = 0.7092$. This represented a significant improvement over the value $\rho_c \sigma^3 = 0.4611$ obtained using the PY pair correlation function and the mean field approximation to the coexistence surface.⁶

In Sec. III we use the exact coexistence curve for the lattice gas with pairwise interactions⁷ and the accurate Carnahan-Starling (CS) approximation to the pair correlation function^{5,8} to yield $\rho_c \sigma^3 = 0.6678$, which is slightly lower than the value obtained using the PY pair correlation function.

In order to assess the accuracy of using the Kirkwood superposition approximation in the present model, in Sec. III we introduce a higher order superposition approximation to the n -body correlation functions which includes not only pair correlation functions but also triplet correlation functions for a

triangle of spheres in mutual contact. The triplet correlation function for three spheres in rolling contact has recently been calculated⁹ using the Percus-Yevick 3 approximation (PY3), which includes triplet correlations.¹⁰ We discovered that the numerical values obtained for the triplet correlation function when all three spheres are in mutual contact are very well approximated by the simple analytical form

$$\frac{g_3^0}{(g_2^0)^2} = \frac{4 - 7\eta + 7\eta^2 - 2\eta^3}{4(1 - \eta)^3}. \quad (1)$$

Here g_3^0 and g_2^0 are the triplet and pair correlation functions for spheres in contact, and $\eta = (\pi/6)\rho\sigma^3$ is the packing fraction.

Within the above approximation for the n-body correlation functions, the adsorption model is equivalent to a two-dimensional lattice gas with both pairwise and three-body interactions which is itself equivalent to an Ising model with two-spin and three-spin interactions. The interface method of Müller-Hartmann and Zittarz,¹¹ which approximates the interface free energy of a two-dimensional Ising model by considering only a restricted class of possible configurations, has been used to calculate the critical point, at which the interface free energy vanishes, for an Ising model on the triangular lattice with both two-spin and three-spin interactions.¹² For the equivalent lattice gas, this estimate of the critical point together with Eq. (1) yielded the critical density $\rho_c\sigma^3 = 0.8409$, which is substantially higher than the value obtained using the Kirkwood superposition approximation and the lattice gas with only pairwise interactions. Triplet correlations in the fluid are thus important and can significantly affect the phase behavior at the fluid-crystal interface in the present model.

II. The Model

We consider a three-dimensional model for adsorption^{1,2,6} which consists of a fluid of N hard spheres of diameter σ in a container of volume V with a hard, planar wall at $z = -\sigma/2$. A triangular lattice of sticky adsorption sites with first neighbor separation σ is located on the wall. The coordinate system is chosen so that the contact plane for adsorption of a sphere on the wall is at $z = 0$, and an associated triangular lattice Λ is located at the contact plane such that if the center of a sphere is at a site of Λ , then the sphere is in contact with a sticky site on the wall.

The potential $U^s(\mathbf{r}_i)$ for the interaction of a sphere i at \mathbf{r}_i with the sticky sites is given as

$$e^{-\beta U^s(\mathbf{r}_i)} = 1 + \lambda \sum_{\mathbf{R}_s \in \Lambda} \delta(\mathbf{r}_i - \mathbf{R}_s), \quad (2)$$

where $\beta = (kT)^{-1}$, δ is the Dirac delta function, and λ is a stickiness parameter. The positions of sites on the triangular lattice Λ at the contact plane are represented by \mathbf{R}_s .

The Hamiltonian for the system can be written as

$$H = H_0 + H_S, \quad (3)$$

where H_0 is the Hamiltonian for the system without the sticky sites (the smooth wall problem), and

$$H_S = \sum_{i=1}^N U^s(\mathbf{r}_i). \quad (4)$$

The canonical partition function for the system is given as

$$Z = \frac{1}{N!} \int d\mathbf{r}^N e^{-\beta H}. \quad (5)$$

After integrating to remove the delta functions and grouping terms, we obtain

$$Z/Z_0 = \sum_{n=0}^N \frac{\lambda^n}{n!} \sum_{\{\mathbf{R}_i\} \subset \Lambda} \rho_n^0(\mathbf{R}_1, \dots, \mathbf{R}_n), \quad (6)$$

where Z_0 is the partition function for the smooth wall problem, and

$$\begin{aligned} \rho_n^0(\mathbf{r}_1, \dots, \mathbf{r}_n) &= [Z_0(N-n)!]^{-1} \int d\mathbf{r}_{n+1} \dots d\mathbf{r}_N e^{-\beta H_0} \\ &= g_n^0(\mathbf{r}_1, \dots, \mathbf{r}_n) \prod_{i=1}^n \rho_1^0(\mathbf{r}_i). \end{aligned} \quad (7)$$

Here $g_n^0(\mathbf{r}_1, \dots, \mathbf{r}_n)$ is the n -body correlation function and $\rho_1^0(\mathbf{r}_i)$ is the single particle density for the smooth wall problem, for which $\rho_1^0(\mathbf{r}_i) = \rho_1^0(z_i)$. Thus

$$Z/Z_0 = \sum_{n=0}^N \frac{[\lambda \rho_1^0(0)]^n}{n!} \sum_{\{\mathbf{R}_i\} \subset \Lambda} g_n^0(\mathbf{R}_1, \dots, \mathbf{R}_n). \quad (8)$$

We then define the potential of mean force $U(\mathbf{R}_1, \dots, \mathbf{R}_n)$ as

$$g_n^0(\mathbf{R}_1, \dots, \mathbf{R}_n) = e^{-\beta U(\mathbf{R}_1, \dots, \mathbf{R}_n)}. \quad (9)$$

We shall approximate $U(\mathbf{R}_1, \dots, \mathbf{R}_n)$ as

$$U(\mathbf{R}_1, \dots, \mathbf{R}_n) = \sum_{nn} W + \sum_{\Delta} W_3, \quad (10)$$

where W is the potential of mean force for a pair of spheres in contact on a pair of sites on Λ , and $W_3 + 3W$ is the potential of mean force for three spheres in mutual contact on a triangle of sites on Λ . The first sum in Eq. (10) is over first neighbor pairs of sites in $\{\mathbf{R}_1, \dots, \mathbf{R}_n\}$, and the second sum is over triangles of first neighbor sites in $\{\mathbf{R}_1, \dots, \mathbf{R}_n\}$.

This triplet approximation to the potential of mean force is thus equivalent to the superposition approximation

$$g_n^0(\mathbf{R}_1, \dots, \mathbf{R}_n) = \prod_{nn} g_2^0 \prod_{\Delta} \frac{g_3^0}{(g_2^0)^3}, \quad (11)$$

where

$$\begin{aligned} g_2^0 &= e^{-\beta W}, \\ g_3^0 / (g_2^0)^3 &= e^{-\beta W_3}. \end{aligned} \quad (12)$$

Here, g_2^0 is the contact pair correlation function for the smooth wall problem for a pair of spheres on a pair of first neighbor sites on Λ , and g_3^0 is the contact triplet correlation function for three spheres on an equilateral triangle of first neighbor sites on Λ . The superposition approximation of Eq. (11) differs from the Kirkwood superposition approximation³ used in earlier papers^{1,2,6} which did not include triplet correlations on the triangles of first neighbor sites.

Substituting Eq. (9) and Eq. (10) into Eq. (8) and changing from a sum over the positions of labelled spheres on Λ to a sum over lattice sites of Λ yields

$$Z/Z_0 = \sum_{\{t_i\}} e^{\beta\mu\sum_{i\in\Lambda} t_i} e^{-\beta W\sum_{nn} t_i t_j} e^{-\beta W_3\sum_{\Delta} t_i t_j t_k}, \quad (13)$$

where t_i is the occupation number of lattice site i , and where

$$\lambda\rho_1^0(0) = e^{\beta\mu}. \quad (14)$$

Thus $Z/Z_0 = \Xi$, the grand canonical partition function for a lattice gas of spheres on Λ which have a chemical potential μ , a nearest neighbor pairwise interaction W , and a three-body interaction W_3 on triangles of nearest neighbor sites.

III. Estimates of the Minimum Density for Two-Phase Coexistence

The fraction of sites of Λ which are occupied by spheres is given as ^{1,2,6}

$$\theta = \frac{\lambda}{|\Lambda|} \frac{\partial}{\partial \lambda} \ln \Xi. \quad (15)$$

The simplest approximation is to assume the lattice gas has no lateral interactions; i.e., $W = W_3 = 0$. Eqs. (13) - (15) then give the Langmuir adsorption isotherm¹³

$$\theta = \frac{\lambda\rho_1^0(0)}{1 + \lambda\rho_1^0(0)}. \quad (16)$$

Without the presence of lateral interactions, no phase transition is predicted to occur at the contact plane.

The next higher approximation is to assume that there are only pairwise lateral attractions in the lattice gas; i.e., $W < 0$ and $W_3 = 0$. The two-phase

coexistence curve and the adsorption isotherms can be calculated numerically within the mean field approximation. This approximation predicts the critical point of the condensation transition to be given as⁶

$$\begin{aligned} -(\beta W)_c &= 2/3 \\ (g_2^0)_c &= e^{2/3} = 1.9477. \end{aligned} \tag{17}$$

Using the PY virial approximation to the pair correlation function⁴⁻⁶

$$g_2^0 = \frac{1 + \eta/2}{(1 - \eta)^2}, \tag{18}$$

where $\eta = (\pi/6)\rho\sigma^3$ is the packing fraction, yields the estimate $\rho_c\sigma^3 = 0.4611$ of the fluid density at the critical point of the condensation transition at the contact plane.⁶

For the case of pair interactions in two dimensions, the two-phase coexistence surface is known exactly,^{2,7} and highly accurate approximations to the adsorption isotherms can be constructed.¹³ The critical point occurs on the exact coexistence curve for the case of pairwise interactions on the triangular lattice at^{2,14}

$$(g_2^0)_c = 3. \tag{19}$$

The PY pair correlation function of Eq. (18) then yields the estimate $\rho_c\sigma^3 = 0.7092$ for the fluid density at the critical point of the phase transition at the contact plane.² This estimate is a significant improvement over the value of the critical density obtained using the mean field approximation to the coexistence surface.

If this minimum fluid density for a phase transition is calculated using Eq. (19) and the highly accurate CS pair correlation function,^{5,8}

$$g_2^0 = \frac{1 - \eta/2}{(1 - \eta)^3}, \quad (20)$$

the estimate $\rho_c \sigma^3 = 0.6678$ is obtained, which differs only slightly from the value obtained using the PY pair correlation function.

The next higher approximation, which is the central focus of the present paper, is to assume both W and W_3 are non-zero.

For an Ising model on the triangular lattice with the Hamiltonian ($s_i = \pm 1$, $J_3 > 0$)

$$\mathcal{H} = J \sum_{\langle ij \rangle} s_i s_j + J_3 \sum_{\langle ijk \rangle} s_i s_j s_k - h \sum_i s_i, \quad (21)$$

the critical point for the ferromagnetic ($J < 0$) case was calculated¹² using the accurate interface method of Müller-Hartmann and Zittarz¹¹ to be given as $\exp(-4\beta J)_c = 3$, so long as the three spin interaction on a triangle of sites was bounded as $J_3 < 3|J|/2$.

This Ising model is equivalent to the lattice gas of Eq. (13) with $W = 4J - 8J_3$ and $W_3 = 8J_3$. The critical point for condensation in this lattice gas is then given as, letting $g_0 = g_3^0/(g_2^0)^2$,

$$(g_0)_c = 3 \quad (22)$$

so long as $W_3 < -3W/4$, which is equivalent to $g_0 > (g_2^0)^{1/4}$.

For the case of three spheres in mutual contact, g_0 has been calculated numerically using the PY3 approximation¹⁰ by Attard and Stell.⁹ The values they obtained for several fluid densities are given in Table 1.⁹ Using the CS formula for g_2^0 , it is easy to see that $g_0 > (g_2^0)^{1/4}$ is satisfied for all densities studied. Using the

CS formula for g_2^0 and the PY3 values for g_0 , it is also clear that $W_3 > 0$.

For the case of three spheres in mutual contact, Attard has proposed the simple approximation¹⁵

$$g_0 = (g_2^0 + 1)/2 . \quad (23)$$

We used the PY and CS approximations for g_2^0 together with Eq. (23) and discovered the approximate relationship

$$g_0^{\text{CS}} \cong (g_0^{\text{PY}} + g_0^{\text{PY3}})/2 . \quad (24)$$

Eq. (24) then yields the simple closed-form approximation $g_0^{\text{PY3}} \cong g_0^*$, where

$$g_0^* = \frac{4 - 7\eta + 7\eta^2 - 2\eta^3}{4(1 - \eta)^3} . \quad (25)$$

Values of g_0^* calculated using Eq. (25) are given in Table 1 and compare very well with the PY3 values.⁹

Using Eq. (22) and Eq. (25), we obtain the estimate $\rho_c \sigma^3 = 0.8409$ of the minimum fluid density necessary for a phase transition to occur at the contact plane. This estimate differs substantially from that given by the lattice gas with only pair interactions and indicates that the inclusion of triplet correlations for three spheres in mutual contact is important for the study of adsorption phenomena using the model described in Sec. II. Since the inclusion of triplet correlations in the model resulted in a repulsive ($W_3 > 0$) three-body interaction in the equivalent lattice gas, it is understandable that the resulting estimate of the minimum fluid density necessary for a phase transition is larger than that previously predicted using only the effects of pair correlations.

The effects of triplet correlations for other configurations of three spheres on the triangular lattice can be neglected, however, for the calculations of Attard and Stell⁹ of the triplet correlation function for the general case of three spheres in rolling contact can be used to show that the three-body interaction energies in the equivalent lattice gas which result from these other configurations are negligibly small. As a result, the value $\rho_c \sigma^3 = 0.8409$, which includes the correlations of three spheres in mutual contact, should be a good estimate of the location of the critical point of the phase transition.

Monte Carlo computer simulations have been performed for a similar model,¹⁴ one in which the sticky sites are replaced by small sticky regions in order to facilitate the adsorption of a significant number of hard spheres in a reasonable number of Monte Carlo steps. These Monte Carlo results indicated that three-body correlations may be quite important at high densities. This is certainly consistent with the results of the present theoretical investigation.

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Table 1. Comparison of g_0^* values calculated using the closed form approximation of Eq. (25) to the accurate numerical values of g_0^{PY3} obtained by Attard and Stell.⁹

$\rho\sigma^3$	g_0^*	g_0^{PY3}	error
0.1	1.0730	1.0713	0.2%
0.2	1.1641	1.1610	0.3%
0.3	1.2796	1.2753	0.3%
0.4	1.4282	1.4225	0.4%
0.5	1.6228	1.6164	0.4%
0.6	1.883	1.878	0.3%
0.7	2.239	2.238	0.04%
0.8	2.738	2.751	0.5%
0.9	3.46	3.52	1.7%